

ADDITIVE EFFECTS OF SOLVENT REFINED COAL FRACTIONS AND
NITROGEN-CONTAINING AROMATIC COMPOUNDS ON THE
HYDROGENOLYSIS OF THE DIARYLMETHANE

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INTRODUCTION

The authors have already reported that solvent refined coal (SRC) promotes the hydrogenation of aromatic compounds in tetralin [1]. Further investigation has revealed that SRC not only donates its inherent hydrogen but mediates the hydrogen transfer from tetralin to the diarylmethane [2]. The structural analysis of SRC was monitored, and some imino linkages in SRC were suggested to be the possible moiety shuttling hydrogen.

This paper intended to clarify the action mechanism of SRC in hydrogen transfer reactions and presented the SRC-mimetic hydrogenolysis of the diarylmethane.

EXPERIMENTAL

Materials

The diarylmethanes were synthesized according to the method described in the previous paper [3]. The additives and the solvents were commercially purchased and purified if necessary by the conventional methods. The SRC's were prepared from Miike (C, 84.5%, H, 6.1%), Akabira (C, 83.4%, H, 6.2%), and Yallourn (C, 67.4%, H, 5.9%) coals as follows: each coal (20 g) was reacted in tetralin (60 ml) at 400 °C at 9.0 MPa of hydrogen for 30 min. The reaction mixtures were subjected to Soxhlet extraction for 15 h using tetrahydrofuran (THF) as solvent. The residues obtained in the reduced distillation (3 mmHg, at 250°C, for 1 h) of the THF extracts were used as SRC in the hydrogenolysis of the diarylmethane. Column chromatographic separation of SRC derived from Miike Coal, which would be designated only as SRC unless otherwise noted, was carried out by eluting ether-MeOH (98:2 v/v) (SRC-1, 54 wt%), THF (SRC-2, 38 wt%), and pyridine (SRC-3, 8 wt%). Table 1 shows the elemental analyses of the SRC's.

Hydrogenolysis of the diarylmethane

Prescribed amounts of a diarylmethane, a hydrogen donor solvent, and an additive were put into a 90 ml stainless, magnetically stirred autoclave. After being pressurized by 2.0 MPa of hydrogen, the autoclave was heated up to the reaction temperature and maintained during the prescribed period of time. After the reaction, the autoclave was cooled to room temperature by an electric fan.

Product analysis

The products were identified by GC-MS. Quantitative analysis of the products recovered with THF was carried out by GC. Structural change of SRC was monitored by means of ¹H- and ¹³C-NMR, GPC, and elemental analysis.

RESULTS AND DISCUSSION

Solvent-dependent additive effect of SRC

As Table 2 shows, addition of SRC promotes the hydrogenolysis of di(1-naphthyl)methane. The additive effect does not seem to depend on SRC origin, reflecting their similar chemical compositions [4], but it is greatly affected by the hydrogen donatability of solvent. On addition of Yallourn or Akabira SRC (0.40 g), about a two-fold larger conversion of di(1-naphthyl)methane is obtained in tetralin than in 1-methylnaphthalene, respectively.

The additive effect of recovered SRC is also solvent dependent (Table 3). In tetralin, recovered SRC and raw SRC show the comparable additive effect and the similar conversion of tetralin is obtained. Under the reaction conditions, the rearrangement of tetralin to 1-methylindan also occurred and the molar ratio of 1-methylindan/naphthalene was 3.05 in the absence of SRC. This ratio decreased to 0.86-1.10 in the presence of SRC. These facts suggest that the initial transfer of α -hydrogen in tetralin would occur more selectively in the presence of SRC since 1-methylindan is derived only from 2-tetralyl radical and isomerization of 1- and 2-tetralyl radicals is negligible [5]. Recovered SRC, which was partly dehydrogenated in the first reaction, showed the comparable promoting effect compared with raw SRC. This fact suggests that hydrogen shuttling could occur on the dehydrogenated moiety in the recovered SRC. On the other hand, in 1-methylnaphthalene, a modest conversion of 9-benzylphenanthrene is obtained in the presence or absence of recovered SRC, suggesting that almost no hydrogen transfer proceeds from 1-methylnaphthalene or decalin to dehydrogenated SRC.

Tables 4 and 5 show that the conversion of di(1-naphthyl)methane does not necessarily correlate with the amount of H_{α} in the fractionated SRC. The weight ratio of hydrogen consumed in the hydrogenolysis of di(1-naphthyl)methane/ H_{α} lost from SRC falls on 1.8-5.7, which reinforces that some bondings in dehydrogenated SRC act as a hydrogen shuttler rather than a hydrogen donor as shown in Scheme 1.

Structural analysis of SRC

Figure 1 shows the GPC profiles of the raw and recovered SRC's. Basically, similar molecular size distributions were obtained before and after the reactions for all the SRC's although the structures sensitive to light at 260 nm grew for SRC-3 after the reaction. These findings indicate that decomposition and condensation of SRC are negligible under the reaction conditions. Thus, the recovered SRC was analyzed by ^{13}C -NMR in order to detect the chemical structures shuttling hydrogen in dehydrogenated SRC. Figure 2 shows the ^{13}C -NMR spectrum of the recovered SRC soluble in THF. The carbon atoms at 139 and 154 ppm can be assigned to the azomethine carbons and the carbons at the ipso-positions in phenolics.

This finding urged us to investigate into the hydrogen shuttling

abilities of 3-ring azaaromatic compounds, which have been sparsely documented in the literature. They were also compared with the hydrogen shuttling abilities of some aromatic hydrocarbons.

Hydrogen shuttling effect of some azaaromatics

As Table 6 shows, the hydrogenolysis of 9-benzylphenanthrene is remarkably promoted on adding acridine or phenanthridine. However, 1- and 4-azaphenanthrenes are less effective additives.

These facts can be interpreted on the basis of the hydrogen accepting abilities of these hydrogen shuttlers. It has been reported in our previous paper [3] that the superdelocalizability gives a good measure to estimate the reactivity of the diarylmethane toward hydrogenolysis, and the quantum chemical data in Table 7 also indicate that phenanthridine and acridine are more hydrogen accepting than quinoline, 1-azaphenanthrene, and 4-azaphenanthrene (eqs. (1) and (5) in Fig. 3).

The other factor controlling the effectiveness of the shuttler is the hydrogen releasing ability of the hydroaromatic radical derived from the hydrogen transfer to the azaaromatic compound. If the hydroaromatic radical is more susceptible to further hydrogenation (eqs. (3) and (7)) rather than to hydrogen donation to 9-benzylphenanthrene (eqs. (2) and (6)), considerable amounts of hydrogen from tetralin is consumed in vain to afford the dihydro-derivatives of the shuttlers. The perhydro-derivatives of the azaaromatics are considered to show the lower hydrogen donatability than the hydroaromatic radicals. Direct and indirect overhydrogenation reactions of the shuttler such as disproportionation of these dihydro-derivatives formed in eqs. (3) and (7) are undesirable to promote the smooth hydrogen shuttling.

The azaaromatics used in this study showed the different reactivities toward hydrogenation of their own aromatic nuclei. In the tetralin-acridine system, 87% of acridine was converted to afford 9,10-dihydroacridine and 1,2,3,4-tetrahydroacridine in 18 and 60% selectivities, respectively. As for the tetralin-quinoline system, 52% of quinoline was converted to 1,2,3,4- and 5,6,7,8-tetrahydroquinolines in 69% combined selectivity. On the other hand, in the tetralin-phenanthridine system, the phenanthridine conversion was not more than 10% and 5,6-dihydrophenanthridine was formed in 60% selectivity. Therefore, there is no correlation between the 9-benzylphenanthrene conversion and the amounts of the perhydro-azaaromatics formed during the reactions.

These facts reveal that phenanthridine could act as an effective hydrogen shuttler since overhydrogenation of phenanthridine and adduction of phenanthridine derived compounds into the hydrogenolysates from 9-benzylphenanthrene occur only to a small extent, contrasting with the cases of quinoline-1,2,3,4-tetrahydroquinoline mixtures [6-8].

CONCLUSION

We have shown that SRC and phenanthridine are effective hydrogen shuttlers. The effectiveness of phenanthridine can be ascribed to its facile hydrogen shuttling ability and higher stability under the reaction conditions.

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Table 1 Elemental Analyses of the Fractionated Miike SRC's.

	SRC raw	SRC-1	SRC-2	SRC-3
Eluent Weight %	Ether-Methanol 54	THF 38	Pyridine 8	
C	86.9%	87.6 %	87.1%	78.3 %
H	5.8	5.9	6.0	5.6
N	1.2	1.1	1.1	1.7
O(diff.)	5.9	5.4	5.8	11.5
Ash	0.23			2.9
H/C	0.80	0.81	0.83	0.86

Table 2 Additive Effect of SRC on the Hydrogenolysis of Di(1-naphthyl)methane (DNM).

SRC (Amount/g)	Conv. of DNM	Yield of 1-MN	Solvent (Conv.)	Sel. of 1-MI
None	8%	6%	Tet(8%)	47%
Yallourn(0.1)	13	9	Tet(8)	38
Akabira (0.1)	12	9	Tet(8)	40
Yallourn(0.4)	38	19	Tet(12)	26
Akabira (0.4)	38	20	Tet(12)	26
Miike (0.4)	36	19	Tet(16)	27
None	5		1-MN(0.3)	
Yallourn(0.1)	9		1-MN(3)	
Akabira (0.1)	6		1-MN(2)	
Yallourn(0.4)	17		1-MN(6)	
Akabira (0.4)	20		1-MN(7)	

DNM 7.5 mmol, solvent 75 mmol, 460°C, initial hydrogen pressure 2.0 MPa, 30 min.
Yallourn SRC (C, 83.3%, H, 6.0%), Akabira SRC (C, 86.2%, H, 6.3%), 1-MN = 1-Methylnaphthalene, Tet = Tetralin, 1-MI = 1-Methylindan.

Table 3 Additive Effect of the SRC's Derived from Miike Coal on the Hydrogenolysis of 9-Benzylphenanthrene (9-BP).

Solvent	Additive	Conv. of 9-BP	Selectivities of			Conv. of Solv.	Select. of	
			Tol	Phen	DHP		MI	NpH
Tetralin	none	19%	71%	70%	13%	13%	61%	20%
Tetralin	raw SRC	52	83	88	11	20	38	44
Tetralin	recovered SRC	42	86	75	11	18	44	40
Decalin	none	17	-	75	Nd	7		
Decalin	raw SRC	35	-	90	3	7		
Decalin	recovered SRC	20	-	77	Nd	7		

9-BP 7.5 mmol, solvent 75 mmol, SRC 0.4 g, 430°C, initial hydrogen pressure 2.0 MPa, 5 h.

Tol = Toluene, Phen = Phenanthrene, DHP = 9,10-Dihydrophenanthrene, MI = 1-Methylindan, NpH = Naphthalene. Nd = Not detected.

Table 4 Additive Effect of the Fractionated SRC's Derived from Miike Coal on the Hydrogenolysis of Di(1-naphthyl)methane.

Additive	Conv. of DNM	Yield of 1-MN	Conv. of Tet	Select. of MI
SRC				
none	8%	6%	8%	47%
SRC raw	36	19	16	27
SRC-1	49	33	16	26
SRC-2	41	19	17	26
SRC-3	30	25	10	26

DNM 7.5 mmol, tetralin 75 mmol, SRC 0.4 g, 460°C, initial hydrogen pressure 2.0 MPa, 30 min.

Table 5 Amounts of Hydrogens Bonded to α -Position on the Aromatic Ring in 0.4g of the SRC Derived from Miike Coal.

	H α /mg in Original SRC A	H α /mg in Recovered SRC B	Consumed H α /mg A - B	Amounts of Hydrogen Needed in the Hydrogenolysis of DNM/mg
SRC raw	7.83	4.83	3.00	5.40
SRC-1	7.83	4.92	2.91	6.15
SRC-2	5.92	4.74	1.18	4.95
SRC-3	3.60	3.02	0.58	3.30

Table 6 Hydrogen-shuttling effect of the azaaromatics in the hydrogenolysis of 9-benzylphenanthrene (9-BP).

Additive (mmol)	Conv. of 9-BP(mol%)				Tetralin conv. (mol%)		Select.(mol%)	
	9-BP(mol%)	Tol	Phen	DHP	conv. (mol%)	1-MI	NpH	
None		19	71	70	11	13	61	20
Quinoline (7.5)	22	76	73	9	19	47	36	
1-Azaphenanthrene(7.5)	23	71	a)	8	18	50	27	
4-Azaphenanthrene(7.5)	23	69	72	7	17	52	28	
Phenanthridine (3.3)	25	74	74	9	20	47	34	
Phenanthridine (7.5)	33	65	73	7	23	43	39	
Phenanthridine (15.0)	36	72	76	8	26	33	44	
Phenanthridine (22.5)	37	70	75	8	28	38	43	
Acridine (7.5)	40	76	79	b)	25	37	53	

9-BP 7.5 mmol, tetralin 75 mmol, reaction temperature 430°C, initial hydrogen pressure 2.0 MPa, reaction time 5 h.

a) Not calculated owing to the inseparability of phenanthrene and the perhydro-derivatives of 1-azaphenanthrene.

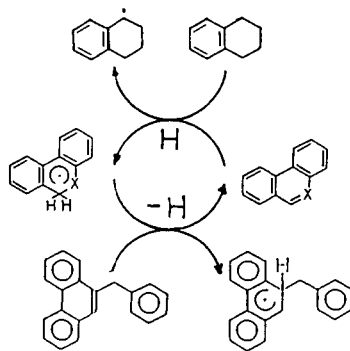
b) Not calculated owing to the inseparability of DHP and the tetra- and octahydroacridines.

Table 7 Superdelocalizability values (Sr(R))^{a)} of some azaaromatics.

Aromatic compounds	Sr(R) (position)
Quinoline	1.0527 (4-)
	1.0059 (5-)
	0.9905 (8-)
Phenanthridine	1.1045 (6-)
	0.9993 (7-)
	0.9936 (5-)
1-Azaphenanthrene	1.0214 (4-)
	1.0009 (5-)
4-Azaphenanthrene	1.0151 (5-)
	0.9926 (6-)
Acridine	1.4732 (9-)
	1.2738 (10-)
	1.0564 (4-)

9-Benzylphenanthrene 0.9803 (9-)

a) Superdelocalizability values toward radical reactions, which were calculated according to the Simple Hückel Theory.



Scheme 1 Hydrogen Shuttling Cycle.

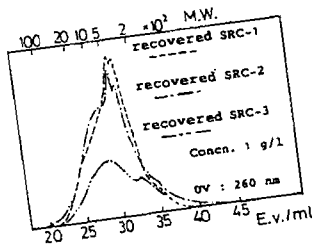
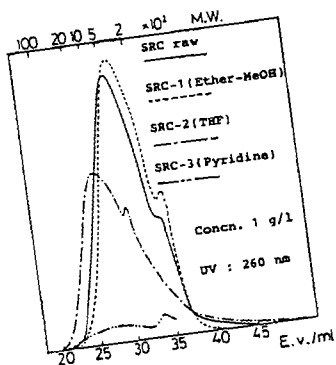


Fig. 1 GPC Profiles of the SRC's.

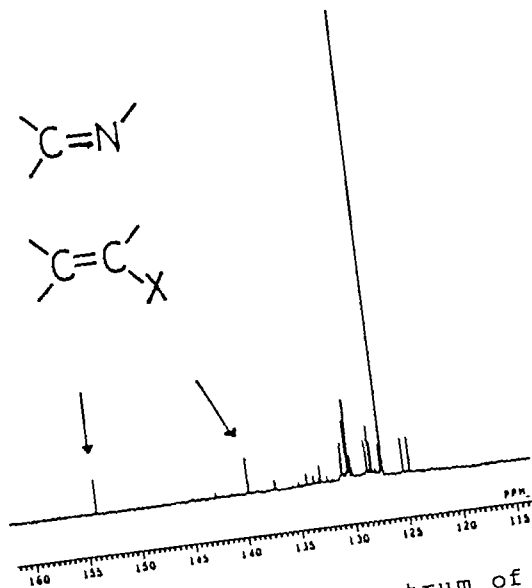
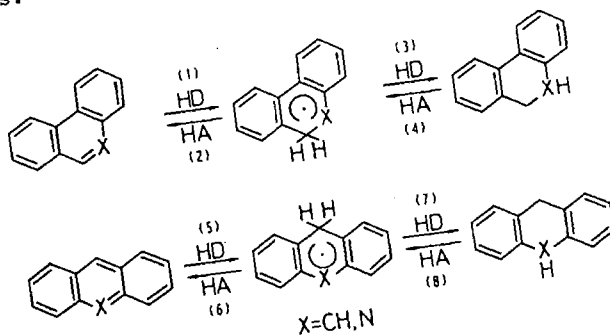


Fig. 2 ^{13}C -NMR Spectrum of the Recovered SRC Soluble in THF-d_8 .



HD=Hydrogen donor
HA=Hydrogen acceptor

Fig. 3 Hydrogen Transfer Processes where the 3-ring Aromatic Compounds and Their Dihydro-derivatives are Involved.